



COMPARISON OF UV PROTECTIVE PROPERTIES OF WOOLLEN FABRICS DYED WITH YELLOW NATURAL DYES FROM DIFFERENT PLANT SOURCES

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ABSTRACT

Woollen fabric treated with tin (II) chloride was dyed using yellow blossoms of different plants in order to compare the UV protection of these yellow dyed fabrics and their ability to eliminate free radicals generated by exposure to UV radiation. All the tested fabrics dyed with different yellow blossoms containing flavonoids or carotenoids showed an excellent protection against UV radiation (low reflectance and transmission of radiation in the near UV radiation, high UPF as well as the ability to eliminate the free radicals formed in contact with UV radiation). The highest level of UV protection was exhibited by the fabric dyed with the blossoms of broom (*Cytisus scoparius*) and dandelion (*Taraxacum officinale*).

KEY WORDS: Natural dyes, dandelion, broom, flavonoids, carotenoids, UV protection.

1. Introduction

Ultraviolet radiation (UV) is a part of the sunlight reaching the Earth's surface. These are electromagnetic waves with a shorter wavelength and higher energy than the wavelength and energy of photons of visible light. 99% of the UV radiation which passes through the earth's atmosphere is composed of UVA radiation (wavelength approximately in the range 315-400 nm). UVA penetrates the skin to a greater extent, which causes damage especially by prolonged exposure. Erythema and stimulation of skin pigmentation occur with much lower intensity than that of UVB radiation. The vast majority of UVB radiation (wavelength range 280-315 nm) is captured in the stratosphere by the ozone layer. A small portion that reaches the earth's surface (UVB), which passes in the attenuated atmosphere of ozone, penetrates into the skin, although a lesser amount than UVA, but it here operates with great efficiency. It is responsible for erythema, stimulating the production of skin pigment (melanin), eye damage (destruction of rods and cones in the retina), disruption of DNA and protein structures in cells and ultimately for skin ageing (photoageing) and an increased incidence of skin cancer. Basic protections against harmful UV radiation include protective glasses, sunscreens and the covering the body with suitable fabrics.

The season of spring in Central Europe is typically represented by a diverse flood of yellow flowers with a maximum flowering in April-May. The function of the first spring flowers is the maximum absorption of sunlight at a time when the night temperature often falls well below freezing. Frequent rain, continuing short days and a lack of sunshine and of pollinating insects represent a much more difficult problem for the pollination of flowers and maturation of seeds. In such conditions, the yellow colour of blossoms is an advantage.

Six of them were randomly selected (yellow blossoms of shrubs and herbs grown in gardens, parks, fields, but also wild) to dye woollen fabrics. This fabric had been previously treated with tin chloride. For dyeing the yellow blossoms of these plants were selected: *Forsythia intermedia*, broom (*Cytisus scoparius*), yellow azalea (*Rhododendron luteum*), *Kerria japonica "Pleniflora"*, rapeseed (*Brassica napus*) and dandelion (*Taraxacum officinale*) (Table 1).

Table 1: Overview of the plants whose yellow blossoms were tested for the dyeing of woollen fabrics

Number	Plant	Latin name	Family	Description	Type of coloured compounds
1	Forsythia	<i>Forsythia intermedia</i>	Oleaceae	shrub, cultivated	flavonoids
2	Broom	<i>Cytisus scoparius</i>	Fabaceae	shrub, wild	flavonoids
3	Yellow azalea	<i>Rhododendron luteum</i>	Ericaceae	shrub, cultivated	flavonoids
4	Kerria	<i>Kerria japonica</i>	Rosaceae	shrub, cultivated	carotenoids
5	Rapeseed	<i>Brassica napus</i>	Brassicaceae	herb, cultivated	carotenoids
6	Dandelion	<i>Taraxacum officinale</i>	Asteraceae	herb, wild	carotenoids

The yellow hue of flowers is derived from flavonoids or carotenoids. Flavonoids are often polyphenolic derivatives of flavone (2-phenyl-1,4-benzopyrone or 2-Phenyl-4H-chromen-4-one, Figure 1) - e.g. apigenin (C.I. 75580) and chrys in broom [Pinela et al., 2011], rutin (C.I. 75730) in forsythia [Rosati et al., 1998], dozens of different flavonoids and anthocyanins in azaleas and rhododendrons [Popescu and Kopp, 2013]. Carotenoids and xanthophylls are other large groups causing yellowish pigments in flowers. They are derivatives of tetraterpene - e.g. carotene (C.I. 75130) and lutein (C.I. 75136, Figure 2) in *Kerria japonica* [Hemalatha et al., 2011] and rapeseed [Reifa et al., 2013] or lutein epoxide in dandelion [Meléndez-Martínez et al., 2006].

The assumption that such dyed fabrics could exhibit high protection against UV radiation comes from the fact that flavonoids and carotenoids are a part of the UV protective system of plants. The yellow surfaces absorb the radiation corresponding to the purple colour that is complementary to the yellow one and the wavelength of purple light (380-420 nm) overlaps already into UVA radiation. Carotenoids and flavonoids are powerful antioxidants and free radical quenchers. The resonance system of conjugated double bonds of these compounds possesses the capacity to absorb short-wave UV light and eliminate the resulting oxygen radicals. The mechanism of their elimination is in both these groups somewhat different: polyphenolic flavonoids act as antioxidants (reductants) which deliver electrons for the quenching of free radicals and form less reactive radicals and quinoid structures. Carotenoids capture and incorporate the radicals into their conjugated system of double bonds to form a resonance stabilised system. There follows fragmentation and formation of epoxides, ketones and various isomers of carotene [Velišek, 1999]. It is possible that the protective effect of the fabric dyed with natural flavonoids and carotenoids could be due to a combination of several factors - UV absorption and elimination of generated free radicals.

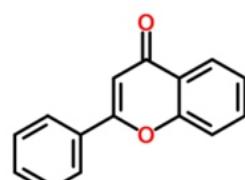


Figure 1: Flavone

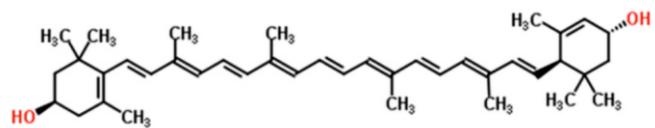


Figure 2: Lutein

Flavonoids and carotenoids are substances that as dietary micronutrients come into light exposed tissues (eyes and skin), there they may cause photo protecting [Stahl and Sies, 2007]. Research is also going on into the topical action of these compounds against photo oxidative damage of the skin, e.g. the active development of *Cytisus scoparius* extract for the potential use in topical applications [González et al., 2013].

2. Experimental

2.1. Materials

Fresh blossoms of these plants and shrubs: *Forsythia intermedia*, broom (*Cytisus scoparius*), yellow azalea (*Rhododendron luteum*), *Kerria japonica* "Pleniflora", rapeseed (*Brassica napus*), dandelion (*Taraxacum officinale*), woollen fabric (surface weight 156 g m⁻²), tin chloride (SnCl₂), Folin-Ciocalteau reagent, sodium carbonate anhydrous (Na₂CO₃), stable radical DPPH (2,2-diphenyl-1-picrylhydrazyl), ethanol.

2.2. Methods

2.2.1. Pre-treatment and dyeing of fabrics

Fabrics were pre-treated with a solution of tin chloride at a concentration of 2 g L⁻¹. This mordant process was performed at a ratio of 1:50 (1 g fabric: 50 ml bath). The bath with the fabric was brought to a boil and then allowed 2 hours spontaneous cooling.

Wringing pre-treated fabrics were transferred into a dyeing bath of distilled water and fresh flowers. Dyeing was executed at a ratio of 1: 100: 20 (1 g fabric: 100 ml of water: 20 g of fresh flowers). The dye bath was brought to a boil and then left for 15 minutes; fabrics were removed from the bath after 12 hours of spontaneous cooling. The dyed fabrics were thoroughly washed using detergent without enzymes, optical brightening, and phosphates and without alkalization and dried at 50 °C. Dyed fabrics were measured on a remission spectrophotometer Datacolor to obtain CIE L*a*b* v colour values and remissions.

2.2.2. UV/VIS spectra of extracts from blossoms

Absorption spectra of the six extracts from blossoms were measured on absorption spectrophotometer UV-1600 PC (Mapada, China), in the region of visible light and near UV radiation.

2.2.3. The content of phenol groups in extracts from blossoms

0.6 g of fresh blossoms of six examined plant species was dosed into glass vessels, each flooded with 20 ml of distilled water, the vessels were sealed and after 10 minutes of boiling the extracts were cooled, filtered and used in analysis to determine the content of the phenol groups using the Folin-Ciocalteau reagent.

The tubes were dosed with 1 ml of distilled water, 1 ml of folic reagent (which was previously diluted 10 times with water), 1 ml of sodium carbonate solution (0.75 M) and 0.2 ml of sample. After 45 minutes the samples were measured with an absorption spectrophotometer (Helios Epsilon, Thermo Scientific) at 735 nm and the absorbance values were compared. Each measurement was carried out 3 times and the average was calculated.

2.2.4. The ability of dyed fabrics to quench free radicals

5 mg of stable free radical DPPH was dissolved in 10 ml of ethanol through stirring. The resulting solution has a dark purple colour with an absorption maximum at a wavelength of about 515 nm. By contact with the antioxidant or substance capable of destroying free radicals the DPPH radical is inactivated, resulting in a different intense colour change from purple to yellow. Samples of dyed fabric were washed, dried, kept 2 hours in a dew chamber with 100% humidity, and then 10 µL of DPPH solution was spotted onto each fabric. The solution penetrated into the fibres treated with dyes (flavonoids and carotenoids) and DPPH was deactivated. Elimination of the radical DPPH showed a varying strength of change of the purple spots towards yellow. The original colour of the fabric and spots from the solution of DPPH were measured after 3 minutes of difference in b* value, which represents a shift in yellow. The greater this difference, the less radical DPPH has been deactivated.

2.2.5. Transmission and UPF

The Ultraviolet Protection Factor (UPF) of clothing was measured using the ultraviolet spectrophotometer Shimadzu UV-3101 PC. This measurement is based on diffuse spectral transmittance in the ultraviolet spectrum of a clothing material as an *in vitro* test.

Transmittance is a value of UVA a UVB radiation which passes through the sample and takes a value of 0-1. Transmittance is expressed in equation (1), where I_0 is the intensity of the incident radiation and I is the radiation coming out of the sample:

$$T = \frac{I}{I_0} \quad (1)$$

Transmittance expressed in % (0-100) is called a transmission.. UPF is calculated as follows (2), where E_λ is CIE erythema spectral effectiveness, S_λ is solar spectral irradiance, T_λ is spectral transmittance and $\Delta\lambda$ is the difference of wavelengths [Hustvedt and Cox Crews, 2005].

$$UPF = \frac{\sum_{290nm}^{400nm} E_\lambda \times S_\lambda \times \Delta\lambda}{\sum_{290nm}^{400nm} E_\lambda \times S_\lambda \times \Delta\lambda \times T_\lambda} \quad (2)$$

E_λ is a standardized function describing the relative sensitivity of erythema to individual wavelengths. It was proposed by McKinlay and Difey (1987) and accepted as a standard by the International Commission on Illumination (CIE). S_λ is the spectral distribution of sunlight falling on the earth's surface (Figure 3) [van Geffen and van der A, 2012].

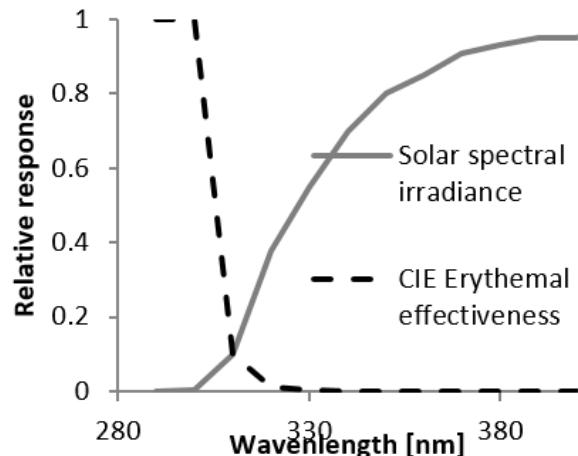


Figure 3: Course of standardized functions E_λ and S_λ

UPF represents the ratio of sunburn-causing UV measured without and with the protection of the fabric. For example, a fabric rated UPF 25 means that, if 25 units of UV fall on the fabric, only 1 unit will pass through to the skin. A UPF 25 fabric that blocks 24 of 25 units of UV is therefore blocking 96 %. Depending on their UPF values, fabrics are divided into groups: very good protection (UPF 25-69) or excellent protection (UPF 40-50+).

3. Results

3.1. Dyeing of woollen fabrics

Table 2 summarizes the results of dyeing (CIE-L*a*b* values of dyed fabrics when using tin mordant at a concentration of 2 g L⁻¹).

As can be seen from Table 2, the lowest brightness value (L*) was measured in samples 1, 2 and 6 (forsythia, broom and dandelion), because their hues were deeper and darker. Positive values of b* indicate a shift to yellow on the blue-yellow axis and a moderate shift to red on the axis of a* (on the red-green axis) was found in samples 2 and 6 (broom and dandelion), however, all six samples had been coloured to nice and clean shades of yellow.

Table 2: L*a*b* values of fabrics dyed with blossoms of plants 1-6 from Table 1 (concentration of SnCl₂ 2 g L⁻¹, mass of blossoms 200 g L⁻¹, length of bath 1:100)

Fabric dyed with	L*	a*	b*
blank	85.3	-1.6	18.4
1	76.9	-0.5	58.1
2	73.8	6.4	72.1
3	79.4	-0.3	39.1
4	80.2	-1.3	37.1
5	80.7	-0.1	63.0
6	76.4	3.6	69.2

(blank = undyed woollen fabric with SnCl₂)

3.2. UV/VIS absorption spectra of extracts from blossoms

Absorption spectra of extracts from blossoms (Figure 4) show a similar course of absorption curves with a maximum around 330-340 nm, which is an area of near UV radiation.

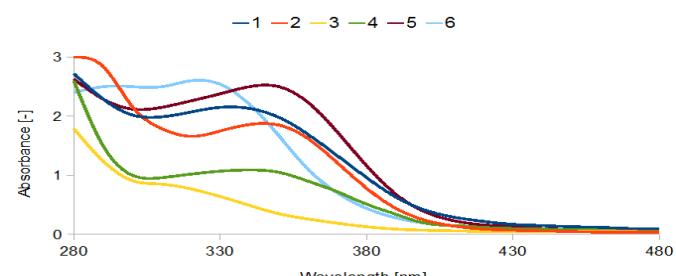


Figure 4: UV/VIS absorption spectra of aqueous extracts from yellow blossoms

3.3. Determination of phenol groups in the extracts and the capacity of dyed fabrics to quench radicals

Table 3 contains an overview of the content of phenol groups in aqueous extracts of the same mass of flowers - marked "Phenols ($A_{765\text{ nm}}$)."¹ It is an absorbance at 736 nm after addition of folinic agent. This value is directly proportional to the total content of phenol groups in flowers.

The dyed fabric was tested with regards to its capacity to quench radicals. It was tested by changing the colour of the fabric caused by the application of DPPH. In the event that the fabric did not respond, the DPPH stain remained purple and Δb^* coordinate in the $L^*a^*b^*$ was a high positive. In the case that fabric quenches all radicals DPPH, Δb^* coordinate in $L^*a^*b^*$ is zero. The results are presented in Table 3.

The highest levels of phenol groups were contained in the extracts from broom and forsythia, the smallest from dandelion. A low content of phenol groups in the extract from the blossoms of dandelion shifted to orange hue of fabrics dyed with dandelion confirm the fact that carotenoid lutein is mainly responsible for the yellow colour of these flowers [6]. The DPPH radical was most strongly deactivated in fabric dyed with azalea (sample 3), dandelion and broom (samples 6 and 2).

Table 3: Comparison of amount of phenols in flowers and dyed fabrics ability to quench free radicals, expressed in colour difference on the colour axis b^* (CIE-Lab system) after application of 10 μL DPPH solution

Sample no.	1	2	3	4	5	6
Phenols ($A_{765\text{ nm}}$)	1.86	1.96	0.93	1.24	0.74	0.53
Δb^*	6.3	2.1	0.1	3.9	5.0	0.4

3.4. Remission, transmission of light and UPF

As shown in the remission curves in the visible light (Figure 5), the values of the remission (reflectance) of light at the dyed fabrics are in 400 to 450 nm very low and therefore there is a strong absorption of radiation in coloured fabrics.

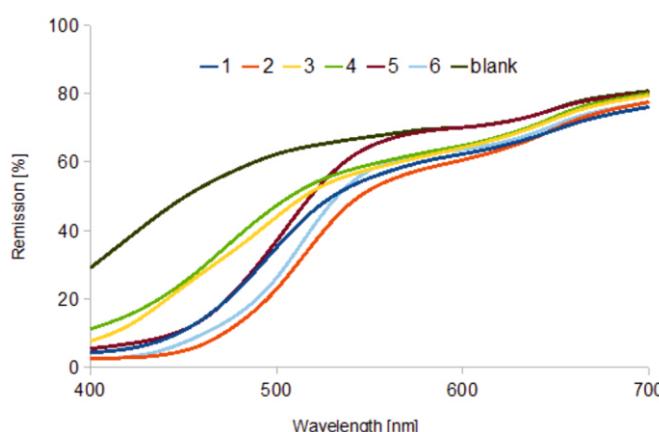


Figure 5: Remission curves of woollen fabric treated only with tin salt (blank) and fabrics dyed with different yellow blossoms

The combination of colour extracts from blossoms with woollen fibres and tin salt form complexes that result in an increasing colour and bathochromic shift (toward longer wavelengths). So while extracts from blossoms themselves absorb mostly wavelengths up to about 380 nm, the pre-treated and dyed fabrics shift the absorption to about 450 nm.

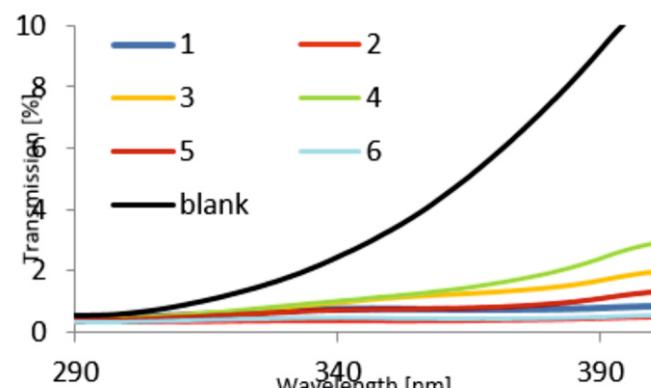


Figure 6: Transmission of light of wavelength 290 to 400 nm of tin-pretreated woollen fabric (blank) and fabrics dyed with different yellow blossoms

Similarly, the light transmissions of wavelength 290 to 400 nm through dyed fabrics were comparable to the undyed fabrics, at very low values (Figure 6). This is associated with the high UPF values (Table 4) which, especially in fabrics dyed with the blossoms of broom and dandelion, highly exceeded the value defined as "excellent UV protection". With regard to woollen fabric used with a high sett, which itself had a UPF 50+ (88.5), all tested samples obviously showed excellent protection, but in Figure 4 there are significant differences between the dyed fabrics, which are reflected in the UPF values (Table 4). While undyed fabric begins transmitting radiation of wavelength around 305 nm, dyed fabrics started to transmit light of wavelength around 330 nm. The resulting colour in the tested samples, had UPF values ranging from 164.7 (azalea) to 319.3 (broom).

Table 4: UPF values of tested dyed woollen fabrics

No.	1	2	3	4	5	6
UPF	186.1	319.3	164.7	173.6	196.4	261.0
blank						88.5

(blank = undyed woollen fabric with SnCl₂)

4. Discussion

The same weight of fresh blossoms (200 g in 1 litre) was used to dye the woollen fabrics pre-treated with tin chloride in a concentration of 2 g L⁻¹. All the blossoms succeeded in colouring the pre-treated woollen fabrics to bright yellow hues, each of which showed an excellent UV protective ability (UPF 50+). The highest UPF values of all tested samples were measured in fabric dyed with flavonoid compounds from blossoms of broom (UPF 319.3), which was e.g. in comparison with fabric dyed with yellow azalea (UPF 164.7) almost double the value. Also the UPF value of fabric dyed with the blossoms of dandelion, whose main ingredient responsible for the yellow colour is the carotenoid lutein, was very high (UPF 261). Its bright rich hue of yellow colour is very similar to the hue of fabric dyed with the blossoms of broom. Also both fabrics even after thorough washing retained (apart from fabric dyed with yellow azalea) the best ability to eliminate free radicals.

5. CONCLUSION

We demonstrated that different yellow blossoms of herbs and shrubs from Central Europe, which naturally contain flavonoids and carotenoids, can be successfully used for the dyeing of woollen fabrics. These blossoms supply, after pre-treatment with tin (II) salt, not only a brilliant yellow colour, but also for the preparation of fabrics with a high UPF, an excellent UV absorption capacity and an ability to eliminate damaging free radicals. The best UPF values were found in fabrics dyed with blossoms of broom and dandelion. These blossoms also demonstrated an excellent ability to destroy free radicals.

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